

WE CLAIM:

1. A nonpolymeric silsesquioxane in which at least one silicon atom is bound to at least one acid-cleavable substituent R^{CL} , wherein the silsesquioxane has a glass transition temperature T_g of greater than 50°C and R^{CL} is cleavable upon exposure to acid at a temperature below T_g .

2. The silsesquioxane of claim 1, wherein R^{CL} is cleavable upon exposure to acid at a temperature that is at least 5°C below T_g .

3. The silsesquioxane of claim 1, selected from: (a) a polyhedral silsesquioxane optionally having one to three open vertices; and (b) a macromer of two to four polyhedral silsesquioxanes that may be the same or different, with each polyhedral silsesquioxane optionally having one to three open vertices.

4. The silsesquioxane of claim 3, wherein the polyhedral silsesquioxane of (a) and the polyhedral silsesquioxanes of (b) have from 4 to 10 faces.

5. The silsesquioxane of claim 1, wherein each silicon atom of the silsesquioxane is covalently bound to a moiety selected from: hydrogen; R^{CL} ; an acid-inert, polar substituent R^P ; and an acid-inert, nonpolar substituent R^{NP} .

6. The silsesquioxane of claim 1, wherein the silsesquioxane is additionally substituted with at least one of R^P and R^{NP} .

7. The silsesquioxane of claim 6, substituted with R^P and optionally R^{NP} .

8. The silsesquioxane of claim 6, substituted with R^{NP} and optionally R^P .

9. The silsesquioxane of claim 1, wherein R^{CL} has the structure



in which:

m, n, and q are independently zero or 1;

r is an integer of at least 1;

L^1 is selected from $-O-SiR^2R^3-$, C_1-C_{12} alkylene, substituted C_1-C_{12} alkylene, C_1-C_{12} heteroalkylene, substituted C_1-C_{12} heteroalkylene, C_5-C_{14} arylene, substituted C_5-C_{14} arylene, C_5-C_{14} heteroarylene, substituted C_5-C_{14} heteroarylene, C_6-C_{14} aralkylene, substituted C_6-C_{14} aralkylene, C_6-C_{14} heteroaralkylene, and substituted C_6-C_{14} heteroaralkylene, wherein R^2 and R^3 are hydrogen or C_1-C_{12} hydrocarbyl, and further wherein when L^1 is optionally substituted and/or heteroatom-containing C_3-C_{12} alkylene, L^1 may be linear, branched, or cyclic;

X is selected from C_3-C_{30} alicyclic and substituted C_3-C_{30} alicyclic;

L^2 is selected from C_1-C_{12} alkylene, substituted C_1-C_{12} alkylene, C_1-C_{12} heteroalkylene, substituted C_1-C_{12} heteroalkylene, C_5-C_{14} arylene, substituted C_5-C_{14} arylene, C_5-C_{14} heteroarylene, substituted C_5-C_{14} heteroarylene, C_6-C_{14} aralkylene, substituted C_6-C_{14} aralkylene, C_6-C_{14} heteroaralkylene, and substituted C_6-C_{14} heteroaralkylene, and further wherein when L^2 is

optionally substituted and/or heteroatom-containing C₃-C₁₂ alkylene, L² may be linear, branched, or cyclic; and

R¹ is selected from acid-cleavable ester, oligomeric ester, ether, carbonate, acetal, ketal, and orthoester substituents.

10. The silsesquioxane of claim 9, wherein:

r is 1 or 2;

L¹ is selected from -O-SiR²R³- and C₁-C₁₂ alkylene;

R² and R³ are hydrogen or C₁-C₆ hydrocarbyl;

X is C₃-C₁₈ alicyclic;

L² is selected from C₁-C₁₂ alkylene, hydroxyl-substituted C₁-C₁₂ alkylene, C₁-C₁₂ fluoroalkylene, and hydroxyl-substituted C₁-C₁₂ fluoroalkylene;

R¹ is selected from -(CO)-O-R⁴, -[Q¹-(CO)-O]_h-R⁵, -O-R⁶, and -O-(CO)-O-R⁷;

h is an integer in the range of 2 to 8 inclusive;

Q¹ is C₁-C₁₂ alkylene or C₁-C₁₂ fluoroalkylene;

R⁴ and R⁶ are selected from (a) hydrocarbyl substituents with a tertiary carbon attachment point, (b) substituents having the structure -CR⁸R⁹-O-CR¹⁰R¹¹R¹², and (c) substituents having the structure -CR¹³(OR¹⁴)₂;

R⁵, R⁷, and R¹⁴ are selected from C₄-C₁₂ hydrocarbyl, substituted C₄-C₁₂ hydrocarbyl, heteroatom-containing C₄-C₁₂ hydrocarbyl, and substituted heteroatom-containing C₄-C₁₂ hydrocarbyl; and

R⁸, R⁹, R¹⁰, R¹¹, R¹², and R¹³ are independently selected from hydrogen, C₄-C₁₂ hydrocarbyl, substituted C₄-C₁₂ hydrocarbyl, heteroatom-containing C₄-C₁₂ hydrocarbyl, and

substituted heteroatom-containing C₄-C₁₂ hydrocarbyl, and further wherein any two of R⁸, R⁹, R¹⁰, R¹¹, and R¹² may be linked to form a three- to eight-membered cyclic group.

11. The silsesquioxane of claim 10, wherein:

L¹ is selected from -O-SiR²R³- and C₁-C₆ alkylene;

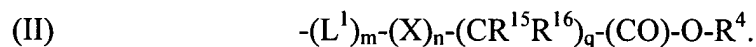
R² and R³ are hydrogen or C₁-C₆ alkyl;

X is C₆-C₁₂ alicyclic; and

L² is of the formula -CR¹⁵R¹⁶- wherein R¹⁵ is hydrogen, C₁-C₁₂ alkyl, or C₁-C₁₂ fluoroalkyl, and R¹⁶ is C₁-C₁₂ alkyl or C₁-C₁₂ fluoroalkyl.

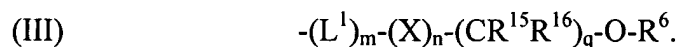
12. The silsesquioxane of claim 11, wherein:

R¹ is of the formula -(CO)-O-R⁴, wherein R⁴ is selected from cyclic and acyclic hydrocarbyl substituents with a tertiary carbon attachment point, such that when r is 1, then R^{CL} has the structure



13. The silsesquioxane of claim 11, wherein:

R¹ is of the formula -O-R⁶, wherein R⁶ is selected from cyclic and acyclic hydrocarbyl substituents with a tertiary carbon attachment point, such that when r is 1, then R^{CL} has the structure



14. The silsesquioxane of claim 12, wherein R⁴ is selected from t-butyl, adamantyl, norbornyl, isobornyl, 2-methyl-2-adamantyl, 2-methyl-2-isobornyl, 2-methyl-2-tetracyclododecenyl, 2-methyl-2-dihydrodicyclo-pentadienyl-cyclohexyl, 1-methylcyclohexyl, 1-methylcyclopentyl, tetrahydropyranyl (THP), tetrahydrofuranyl (THF), 1-ethoxyethyl, 1-methoxy-cyclohexyl, and 1-methoxypropyl.

15. The silsesquioxane of claim 13, wherein R⁶ is selected from t-butyl, adamantyl, norbornyl, isobornyl, 2-methyl-2-adamantyl, 2-methyl-2-isobornyl, 2-methyl-2-tetracyclododecenyl, 2-methyl-2-dihydrodicyclo-pentadienyl-cyclohexyl, 1-methylcyclohexyl, 1-methylcyclopentyl, tetrahydropyranyl (THP), tetrahydrofuranyl (THF), 1-ethoxyethyl, 1-methoxy-cyclohexyl, and 1-methoxypropyl.

16. The silsesquioxane of claim 7, wherein R^P has the structure



in which:

m1, n1, and q1 are independently zero or 1;

L³ is selected from -O-SiR¹⁹R²⁰-, C₁-C₁₂ alkylene, substituted C₁-C₁₂ alkylene, C₁-C₁₂ heteroalkylene, substituted C₁-C₁₂ heteroalkylene, C₅-C₁₄ arylene, substituted C₅-C₁₄ arylene, C₅-C₁₄ heteroarylene, substituted C₅-C₁₄ heteroarylene, C₆-C₁₄ aralkylene, substituted C₆-C₁₄ aralkylene, C₆-C₁₄ heteroaralkylene, and substituted C₆-C₁₄ heteroaralkylene, wherein R¹⁹ and

R^{20} are hydrogen or C_1 - C_{12} hydrocarbyl, and further wherein when L^3 is optionally substituted and/or heteroatom-containing C_3 - C_{12} alkylene, L^1 may be linear, branched, or cyclic;

Y is selected from C_3 - C_{30} alicyclic and substituted C_3 - C_{30} alicyclic;

L^4 is selected from C_1 - C_{12} alkylene, substituted C_1 - C_{12} alkylene, C_1 - C_{12} heteroalkylene, substituted C_1 - C_{12} heteroalkylene, C_5 - C_{14} arylene, substituted C_5 - C_{14} arylene, C_5 - C_{14} heteroarylene, substituted C_5 - C_{14} heteroarylene, C_6 - C_{14} aralkylene, substituted C_6 - C_{14} aralkylene, C_6 - C_{14} heteroaralkylene, and substituted C_6 - C_{14} heteroaralkylene, and further wherein when L^4 is optionally substituted and/or heteroatom-containing C_3 - C_{12} alkylene, L^4 may be linear, branched, or cyclic; and

R^{18} is an acid-inert polar organic group containing a heteroatom with a Pauling electronegativity greater than about 3.00.

17. The silsesquioxane of claim 16, wherein:

L^3 is selected from $-O-SiR^{19}R^{20}-$ and C_1 - C_{12} alkylene;

Y is C_3 - C_{18} alicyclic; and

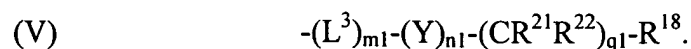
L^4 is selected from C_1 - C_{12} alkylene, hydroxyl-substituted C_1 - C_{12} alkylene, C_1 - C_{12} fluoroalkylene, and hydroxyl-substituted C_1 - C_{12} fluoroalkylene.

18. The silsesquioxane of claim 17, wherein:

L^3 is selected from $-O-SiR^{19}R^{20}-$ and C_1 - C_6 alkylene;

Y is C_6 - C_{12} alicyclic; and

L^4 is of the formula $-CR^{21}CR^{22}-$ wherein R^{21} is hydrogen, C_1 - C_{12} alkyl, or C_1 - C_{12} fluoroalkyl, and R^{22} is C_1 - C_{12} alkyl or C_1 - C_{12} fluoroalkyl, such that R^P has the structure



19. The silsesquioxane of claim 18, wherein the heteroatom within R^{18} is O or N.

20. The silsesquioxane of claim 19, wherein R^{18} is selected from hydroxyl, carboxyl, C_1 - C_{12} alkoxy, C_1 - C_{12} fluoroalkoxy, hydroxyl-substituted C_1 - C_{12} alkoxy, hydroxyl-substituted C_1 - C_{12} fluoroalkoxy, C_2 - C_{12} alkoxyalkyl, fluorinated C_2 - C_{12} alkoxyalkyl, hydroxyl-substituted C_2 - C_{12} alkoxyalkyl, fluorinated hydroxyl-substituted C_2 - C_{12} alkoxyalkyl, hydroxyl-substituted C_1 - C_{12} alkyl, hydroxyl-substituted C_1 - C_{12} fluoroalkyl, carboxyl-substituted C_1 - C_{12} alkyl, carboxyl-substituted C_1 - C_{12} fluoroalkyl, C_2 - C_{12} acyl, fluorinated C_2 - C_{12} acyl, hydroxyl-substituted C_2 - C_{12} acyl, fluorinated hydroxyl-substituted C_2 - C_{12} acyl, C_2 - C_{12} acyloxy, fluorinated C_2 - C_{12} acyloxy, hydroxyl-substituted C_2 - C_{12} acyloxy, fluorinated hydroxyl-substituted C_2 - C_{12} acyloxy, amino, mono- and di- $(C_1$ - C_{12} alkyl)-substituted amino, amido, mono- and di- $(C_2$ - C_{12} alkyl)amido, sulfonamido, N-heteroalicyclic, oxo-substituted N-heterocyclic, and, where the substituents permit, combinations of two or more of the foregoing.

21. The silsesquioxane of claim 20, wherein R^{18} is hydroxyl.

22. The silsesquioxane of claim 19, wherein n is 1.

23. The silsesquioxane of claim 22, wherein q is zero.

24. The silsesquioxane of claim 8, wherein R^{NP} is C_1 - C_{18} hydrocarbyl or fluorinated C_1 - C_{18} hydrocarbyl.

25. A lithographic photoresist composition comprising a photoacid generator and a nonpolymeric silsesquioxane in which at least one silicon atom is bound to an acid-cleavable substituent R^{CL} , wherein the silsesquioxane has a glass transition temperature T_g of greater than 50°C and R^{CL} is cleavable upon exposure to acid at a temperature below T_g .

26. The composition of claim 25, wherein R^{CL} is cleavable upon exposure to acid at a temperature that is at least 5°C below T_g .

27. The composition of claim 25, selected from: (a) a polyhedral silsesquioxane optionally having one to three open vertices; and (b) a macromer of two to four polyhedral silsesquioxanes that may be the same or different, with each polyhedral silsesquioxane optionally having one to three open vertices.

28. The composition of claim 27, wherein the polyhedral silsesquioxane of (a) and the polyhedral silsesquioxanes of (b) have from 4 to 10 faces.

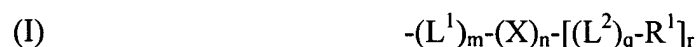
29. The composition of claim 25, wherein each silicon atom of the silsesquioxane is covalently bound to a moiety selected from: hydrogen; R^{CL} ; an acid-inert, polar substituent R^P ; and an acid-inert, nonpolar substituent R^{NP} .

30. The composition of claim 25, wherein the silsesquioxane is additionally substituted with at least one of R^P and R^{NP} .

31. The composition of claim 30, substituted with R^P and optionally R^{NP} .

32. The composition of claim 30, substituted with R^{NP} and optionally R^P .

33. The composition of claim 25, wherein R^{CL} has the structure



in which:

m, n, and q are independently zero or 1;

r is an integer of at least 1;

L^1 is selected from $-O-SiR^2R^3-$, C_1-C_{12} alkylene, substituted C_1-C_{12} alkylene, C_1-C_{12} heteroalkylene, substituted C_1-C_{12} heteroalkylene, C_5-C_{14} arylene, substituted C_5-C_{14} arylene, C_5-C_{14} heteroarylene, substituted C_5-C_{14} heteroarylene, C_6-C_{14} aralkylene, substituted C_6-C_{14} aralkylene, C_6-C_{14} heteroaralkylene, and substituted C_6-C_{14} heteroaralkylene, wherein R^2 and R^3 are hydrogen or C_1-C_{12} hydrocarbyl, and further wherein when L^1 is optionally substituted and/or heteroatom-containing C_3-C_{12} alkylene, L^1 may be linear, branched, or cyclic;

X is selected from C_3-C_{30} alicyclic and substituted C_3-C_{30} alicyclic;

L^2 is selected from C_1-C_{12} alkylene, substituted C_1-C_{12} alkylene, C_1-C_{12} heteroalkylene, substituted C_1-C_{12} heteroalkylene, C_5-C_{14} arylene, substituted C_5-C_{14} arylene, C_5-C_{14}

heteroarylene, substituted C₅-C₁₄ heteroarylene, C₆-C₁₄ aralkylene, substituted C₆-C₁₄ aralkylene, C₆-C₁₄ heteroaralkylene, and substituted C₆-C₁₄ heteroaralkylene, and further wherein when L² is optionally substituted and/or heteroatom-containing C₃-C₁₂ alkylene, L² may be linear, branched, or cyclic; and

R¹ is selected from acid-cleavable ester, oligomeric ester, ether, carbonate, acetal, ketal, and orthoester substituents.

34. The composition of claim 33, wherein:

r is 1 or 2;

L¹ is selected from -O-SiR²R³- and C₁-C₁₂ alkylene;

R² and R³ are hydrogen or C₁-C₆ hydrocarbyl;

X is C₃-C₁₈ alicyclic;

L² is selected from C₁-C₁₂ alkylene, hydroxyl-substituted C₁-C₁₂ alkylene, C₁-C₁₂ fluoroalkylene, and hydroxyl-substituted C₁-C₁₂ fluoroalkylene; and

R¹ is selected from -(CO)-O-R⁴, -[Q¹-(CO)-O]_h-R⁵, -O-R⁶, and -O-(CO)-O-R⁷;

h is an integer in the range of 2 to 8 inclusive,

Q¹ is C₁-C₁₂ alkylene or C₁-C₁₂ fluoroalkylene,

R⁴ and R⁶ are selected from (a) hydrocarbyl substituents with a tertiary carbon attachment point, (b) substituents having the structure -CR⁸R⁹-O-CR¹⁰R¹¹R¹², and (c) substituents having the structure -CR¹³(OR¹⁴)₂;

R⁵, R⁷, and R¹⁴ are selected from C₄-C₁₂ hydrocarbyl, substituted C₄-C₁₂ hydrocarbyl, heteroatom-containing C₄-C₁₂ hydrocarbyl, and substituted heteroatom-containing C₄-C₁₂ hydrocarbyl; and

$R^8, R^9, R^{10}, R^{11}, R^{12}$, and R^{13} are independently selected from hydrogen, C_4-C_{12} hydrocarbyl, substituted C_4-C_{12} hydrocarbyl, heteroatom-containing C_4-C_{12} hydrocarbyl, and substituted heteroatom-containing C_4-C_{12} hydrocarbyl, and further wherein any two of R^8, R^9, R^{10}, R^{11} , and R^{12} may be linked to form a three- to eight-membered cyclic group.

35. The composition of claim 34, wherein:

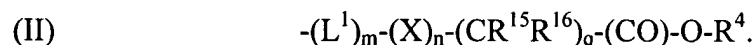
L^1 is selected from $-O-SiR^2R^3-$ and C_1-C_6 alkylene;

R^2 and R^3 are hydrogen or C_1-C_6 alkyl;

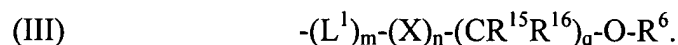
X is C_6-C_{12} alicyclic; and

L^2 is of the formula $-CR^{15}R^{16}-$ wherein R^{15} is hydrogen, C_1-C_{12} alkyl, or C_1-C_{12} fluoroalkyl, and R^{16} is C_1-C_{12} alkyl or C_1-C_{12} fluoroalkyl.

36. The composition of claim 35, wherein R^1 is of the formula $-(CO)-O-R^4$, wherein R^4 is selected from cyclic and acyclic hydrocarbyl substituents with a tertiary carbon attachment point, such that when r is 1, then R^{CL} has the structure



37. The composition of claim 35, wherein R^1 is of the formula $-O-R^6$, wherein R^6 is selected from cyclic and acyclic hydrocarbyl substituents with a tertiary carbon attachment point, such that when r is 1, then R^{CL} has the structure



38. The composition of claim 36, wherein R⁴ is selected from t-butyl, adamantyl, norbornyl, isobornyl, 2-methyl-2-adamantyl, 2-methyl-2-isobornyl, 2-methyl-2-tetracyclododecenyl, 2-methyl-2-dihydrodicyclo-pentadienyl-cyclohexyl, 1-methylcyclohexyl, 1-methylcyclopentyl, tetrahydropyranyl (THP), tetrahydrofuranyl (THF), 1-ethoxyethyl, 1-methoxy-cyclohexyl, and 1-methoxypropyl.

39. The composition of claim 36, wherein R⁶ is selected from t-butyl, adamantyl, norbornyl, isobornyl, 2-methyl-2-adamantyl, 2-methyl-2-isobornyl, 2-methyl-2-tetracyclododecenyl, 2-methyl-2-dihydrodicyclo-pentadienyl-cyclohexyl, 1-methylcyclohexyl, 1-methylcyclopentyl, tetrahydropyranyl (THP), tetrahydrofuranyl (THF), 1-ethoxyethyl, 1-methoxy-cyclohexyl, and 1-methoxypropyl.

40. The composition of claim 31, wherein R^P has the structure



in which:

m1, n1, and q1 are independently zero or 1;

L³ is selected from -O-SiR¹⁹R²⁰-, C₁-C₁₂ alkylene, substituted C₁-C₁₂ alkylene, C₁-C₁₂ heteroalkylene, substituted C₁-C₁₂ heteroalkylene, C₅-C₁₄ arylene, substituted C₅-C₁₄ arylene, C₅-C₁₄ heteroarylene, substituted C₅-C₁₄ heteroarylene, C₆-C₁₄ aralkylene, substituted C₆-C₁₄ aralkylene, C₆-C₁₄ heteroaralkylene, and substituted C₆-C₁₄ heteroaralkylene, wherein R¹⁹ and

R^{20} are hydrogen or C_1 - C_{12} hydrocarbyl, and further wherein when L^3 is optionally substituted and/or heteroatom-containing C_3 - C_{12} alkylene, L^1 may be linear, branched, or cyclic;

Y is selected from C_3 - C_{30} alicyclic and substituted C_3 - C_{30} alicyclic;

L^4 is selected from C_1 - C_{12} alkylene, substituted C_1 - C_{12} alkylene, C_1 - C_{12} heteroalkylene, substituted C_1 - C_{12} heteroalkylene, C_5 - C_{14} arylene, substituted C_5 - C_{14} arylene, C_5 - C_{14} heteroarylene, substituted C_5 - C_{14} heteroarylene, C_6 - C_{14} aralkylene, substituted C_6 - C_{14} aralkylene, C_6 - C_{14} heteroaralkylene, and substituted C_6 - C_{14} heteroaralkylene, and further wherein when L^4 is optionally substituted and/or heteroatom-containing C_3 - C_{12} alkylene, L^4 may be linear, branched, or cyclic; and

R^{18} is an acid-inert polar organic group containing a heteroatom with a Pauling electronegativity greater than about 3.00.

41. The composition of claim 40, wherein:

L^3 is selected from $-O-SiR^{19}R^{20}-$ and C_1 - C_{12} alkylene;

Y is C_3 - C_{18} alicyclic; and

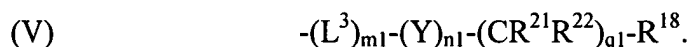
L^4 is selected from C_1 - C_{12} alkylene, hydroxyl-substituted C_1 - C_{12} alkylene, C_1 - C_{12} fluoroalkylene, and hydroxyl-substituted C_1 - C_{12} fluoroalkylene.

42. The composition of claim 41, wherein:

L^3 is selected from $-O-SiR^{19}R^{20}-$ and C_1 - C_6 alkylene;

Y is C_6 - C_{12} alicyclic; and

L^4 is of the formula $-CR^{21}CR^{22}-$ wherein R^{21} is hydrogen, C_1 - C_{12} alkyl, or C_1 - C_{12} fluoroalkyl, and R^{22} is C_1 - C_{12} alkyl or C_1 - C_{12} fluoroalkyl, such that R^P has the structure



43. The composition of claim 42, wherein the heteroatom within R^{18} is O or N.

44. The composition of claim 43, wherein R^{18} is selected from hydroxyl, carboxyl, C_1 - C_{12} alkoxy, C_1 - C_{12} fluoroalkoxy, hydroxyl-substituted C_1 - C_{12} alkoxy, hydroxyl-substituted C_1 - C_{12} fluoroalkoxy, C_2 - C_{12} alkoxyalkyl, fluorinated C_2 - C_{12} alkoxyalkyl, hydroxyl-substituted C_2 - C_{12} alkoxyalkyl, fluorinated hydroxyl-substituted C_2 - C_{12} alkoxyalkyl, hydroxyl-substituted C_1 - C_{12} alkyl, hydroxyl-substituted C_1 - C_{12} fluoroalkyl, carboxyl-substituted C_1 - C_{12} alkyl, carboxyl-substituted C_1 - C_{12} fluoroalkyl, C_2 - C_{12} acyl, fluorinated C_2 - C_{12} acyl, hydroxyl-substituted C_2 - C_{12} acyl, fluorinated hydroxyl-substituted C_2 - C_{12} acyl, C_2 - C_{12} acyloxy, fluorinated C_2 - C_{12} acyloxy, hydroxyl-substituted C_2 - C_{12} acyloxy, fluorinated hydroxyl-substituted C_2 - C_{12} acyloxy, amino, mono- and di- $(C_1$ - C_{12} alkyl)-substituted amino, amido, mono- and di- $(C_2$ - C_{12} alkyl)amido, sulfonamido, N-heteroalicyclic, oxo-substituted N-heterocyclic, and, where the substituents permit, combinations of two or more of the foregoing.

45. The composition of claim 44, wherein R^{18} is hydroxyl.

46. The composition of claim 43, wherein n is 1.

47. The composition of claim 46, wherein q is zero.

48. The composition of claim 32, wherein R^{NP} is C_1 - C_{18} hydrocarbyl or fluorinated C_1 - C_{18} hydrocarbyl.

49. The composition of claim 25, further comprising a dissolution modifying additive.

50. The composition of claim 49, wherein the dissolution modifying additive is a dissolution inhibitor.

51. The composition of claim 25, further comprising a polymer selected to provide transparency at a predetermined wavelength.

52. The composition of claim 51, wherein the polymer is selected from silicon-containing polymers and fluorinated polymers.

53. The composition of claim 25, further comprising a solvent.

54. The composition of claim 25, wherein the photoacid generator is an onium salt selected from sulfonium salts and iodonium salts.

55. A process for patterning a substrate, comprising:

(a) coating a substrate with a photoresist composition comprised of (i) a nonpolymeric silsesquioxane in which at least one silicon atom is bound to an acid-cleavable substituent R^{CL} ,

wherein the silsesquioxane has a glass transition temperature T_g of greater than 50°C, and (ii) a photoacid generator, thereby forming a film;

(b) patternwise exposing the film to an imaging radiation source so as to form a latent, patterned image in the film;

(c) baking the exposed film at a post-exposure bake temperature below T_g ; and

(d) developing the latent image with a developer to form a patterned substrate.

56. The process of claim 55, wherein the nonpolymeric silsesquioxane is selected from:

(a) a polyhedral silsesquioxane optionally having one to three open vertices; and (b) a macromer of two to four polyhedral silsesquioxanes that may be the same or different, with each polyhedral silsesquioxane optionally having one to three open vertices.

57. The process of claim 55, wherein the post-exposure bake temperature is at least 5°C below T_g .

58. The process of claim 57, wherein the post-exposure bake temperature is at least 10°C below T_g .

59. The process of claim 55, further including, subsequent to (a) and prior to (b), baking the coated substrate at a post-application bake temperature in the range of about 90°C to about 150°C.

60. The process of claim 57, further including, subsequent to (a) and prior to (b), baking the coated substrate at a post-application bake temperature in the range of about 90°C to about 150°C.

61. The process of claim 58, further including, subsequent to (a) and prior to (b), baking the coated substrate at a post-application bake temperature in the range of about 80°C to about 120°C.

62. The process of claim 55, wherein the radiation is electron-beam, x-ray, ultraviolet, or extreme ultraviolet radiation.

63. The process of claim 62, wherein the radiation is ultraviolet radiation.

64. The process of claim 63, wherein the ultraviolet radiation has a wavelength of 248 nm, 193 nm, 157 nm, or 13.4 nm.

65. The process of claim 64, wherein the ultraviolet radiation has a wavelength of 193 nm.

66. The process of claim 55, further comprising etching the patterned substrate.

67. The process of claim 66, wherein the etching comprises ion etching.

68. The process of claim 55, wherein the film is insoluble, and wherein the developer renders the film soluble where exposed to the imaging radiation source.

69. The process of claim 68, further comprising removing the soluble film.

70. The process of claim 55, wherein the substrate comprises a silicon wafer, a photolithographic mask blank, or a printed circuit board.

71. The process of claim 55, wherein the substrate coated in (a) has a surface layer of an organic material, such that the patterned substrate is composed of a patterned bilayer resist having an underlayer of the organic material.

72. The process of claim 71, wherein the organic material is selected from diazonaphthoquinone/novolac, polyimides, polyesters, and polyacrylates.

73. The patterned substrate prepared by the process of claim 55.

74. The silsesquioxane of claim 2, wherein R^{CL} is cleavable upon exposure to acid at a temperature that is at least 10°C below T_g .

75. The composition of claim 25, wherein R^{CL} is cleavable upon exposure to acid at a temperature that is at least 10°C below T_g .